ELECTROMECHANICAL PROPERTIES OF POLYETHER-BASED POLYURETHANE COMPOSITES FILLED WITH FUNCTIONALIZED MULTI-WALLED CARBON NANOTUBES

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Introduction

In recent years, electroactive polymers (EAP) have attracted considerable interest, especially following the publication of elevated electric field (E)-induced strain values [1]. The presented results have rendered some specific classes of polymers, such as dielectric and electrostrictive elastomers very attractive for replacing the piezoelectric lead-based ceramics in actuation applications where large displacements are needed for obvious environmental and economic reasons. Besides, in contrast to piezoelectric polymers and ceramics and magnetostrictive ceramics, EAPs are relatively compliant (soft) and capable of extremely large strains (S). In this study, polyether-based polyurethane (PU) films were filled with commercial carboxyl-functionalized multi-walled carbon nanotubes (MWCNT-COOH), in order to improve the electromechanical activities of the matrix. It is well known that a proportional relationship exists between the thickness strain of electrostrictive polymers and the applied E field given by:

$$S \propto \frac{\varepsilon_0 \varepsilon_r'}{Y} E^2 = ME^2 \quad (1),$$ where Y is the Young's

modulus, ε_0 and ε'_r the free space permittivity and the dielectric constant of the polymer, respectively and M is the apparent electrostriction coefficient. So, both ε'_r and Y are the key parameters for controlling EAP actuation and they are generally influenced by fillers in the polymer host.

Thin films of composites were prepared via film casting from viscous solution according to the process described in previous work [2]. At a volume fraction close to the percolation threshold f_C, a remarkable high dielectric constant $\varepsilon'_r \approx 330$ was found, ≈ 50 times higher than the neat PU ($\varepsilon'_r \approx 6$), measured at 0.1 Hz. On the other hand, the stiffness also increased. These two values lead to antagonistic effects on the global electromechanical activity. Thus, an optimum filler fraction (0,8 v%) yielding the maximum electric field-induced strain was found.

Experimental

Materials

The polymer used in this study was a polyether-based aromatic thermoplastic polyurethane (PU), Estane 58888 NAT 021 purchased from Lubrizol Corporation. Carboxyl-functionalized multi-walled carbon nanotubes (MWCNT-COOH), here after also called briefly as CNTC, were purchased from NanoAmor, Inc. The CNTC nanoparticles have a diameter of < 8 nm, a longer between 0.5 – 2 µm. The surface of CNTC was chemically functionalized with ≈ 4 w% –COOH for ease of dispersion into polar solvent.

The composites were cast from separate solutions of PU and CNTC in N,N-dimethylformamide (DMF). Subsequently, the two solutions were mixed together, heated and stirred until a viscous solution was obtained. Then the viscous solution was spread with a film maker (Casting knife, from Elcometer®) forming thin films of ~50 µm thickness and then dried at 60 °C for 1 day. Finally, the obtained films were annealed at 130 °C for 3 hours to eliminate the residual DMF. Samples were cut according to the requirements of the characterization techniques.

Characterization techniques

The dispersion of carbon black was verified by an environmental scanning electron microscopy (FEI XL30 FEG ESEM). The mechanical behavior of the composite films was measured with a multifunctional dynamic mechanical analyzer from Gabo, in simple tensile mode. The complex conductivity was measured with an impedance-meter from Ametek. From this, the dielectric constant ε'_r and the complex electrical conductivity $\sigma*$ could be determined, associated with their loss index. The negative electric field-induced strain *S* was determined at room temperature using a laser interferometer (Agilent 10889B) with a 10 nm precision. A film specimen was positioned between two circular electrodes with 20 mm in diameter to which an alternative electrical voltage was applied at a frequency of 0.1 Hz.

Results and discussion

Fig.1 shows the SEM image of the upper surface of 1v% CNTC/PU film, indicating a rather uniform dispersion of the nano-fillers. The carboxylic groups certainly help to exfoliate the nanotube bundles and dipole-dipole interactions between polar groups of CNTC and PU favor the good dispersion state. Fig.2 gives the variation of the Young's modulus of the composite versus the CNTC content up to 3 v%. As expected, the filler incorporation induces a moderate mechanical

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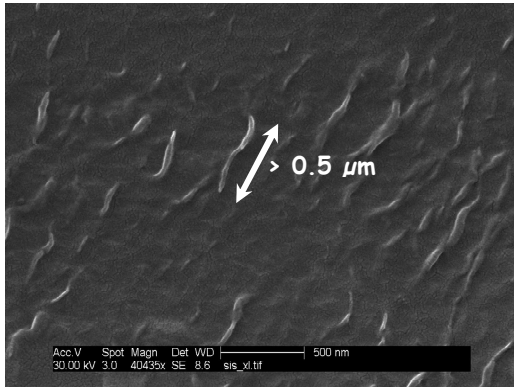reinforcement since Y increases monotonically with CNTC fraction.

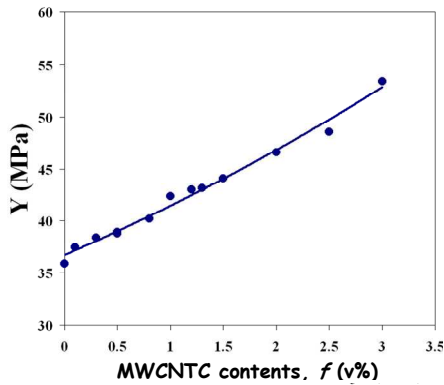Fig.1. Gold-metalized film surface of 1v% CNTC/PU film.

Fig.2. Effect of CNTC concentration on the Young's modulus of PU.

The impact of CNTC fraction on the electric characteristics of the polymer matrix is shown in Fig.3: the dc conductivity, the dielectric constant and the dielectric loss factor (tan δ) all exhibit a large increase when the volume fraction reaches ~1 v%. It corresponds to a classical insulator-conductor transition via a percolation phenomenon. Thus, a five-order of magnitude increase of the dc conductivity is observed. Interestingly, below the percolation threshold f_c lying between 1 and 1,3 v%, the dielectric constant ε'_r can reach high values (330, i.e. a 50-fold increase compared to neat PU) associated to low losses (10). So, the combination of a slight increase of Y modulus, large increase of ε'_r and constant tan δ after filling with ~1v%CNTC should yield an improvement in the electrostriction properties.

Thickness strain measurements at moderate electric field amplitude (E<4V/μm) allowed the determination of the apparent electrostrictive coefficient M, using Eq.(1) (Fig.4). Clearly, absolute values of S and M reach a maximum for f=0,8 v%, fraction close to the percolation threshold f_c. Above 0,8 v%, both –S and –M decrease since the composites progressively lose their dielectric nature during the film compression.
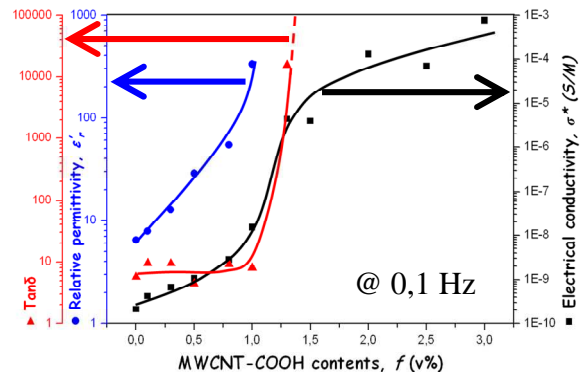

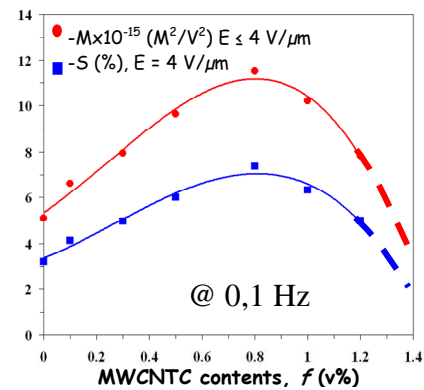Fig.3. Impact of the filler content on the electric properties of polyurethane.

Fig.4. -S and –M at E ≤ 4V/μm versus CNTC.

Conclusion

Polyurethane films filled with carboxyl-functionalized multi-walled carbon nanotubes (CNTC) are interesting composites for electromechanical applications. First, they can be easily prepared via a solution cast method. At last, a small fraction of CNTC (0,8 v%) just below the percolation threshold yields a remarkable increase of the dielectric constant and a slight mechanical reinforcement. Consequently, a beneficial effect was found on the electrostriction coefficient which increased by a factor 2,4 after optimal filling.

References

[1] Guiffard B, Guyomar D, Seveyrat L, et al., Enhanced electroactive properties of polyurethane films loaded with carbon-coated SiC nanowires, *J. Phys. D: Appl. Phys.*, **42**(5) (2009) Article Number: 055503.
[2] Wongtimnoi K, Guiffard B, Bogner-Van de Moortèle A, Seveyrat L, Gauthier C, Cavaillé J-Y. Improvement of electrostrictive properties of a polyether-based polyurethane elastomer filled with conductive carbon black, *Composites Science and Technology*, **71** (2011) 885-892.

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